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Gas Permeation Properties of Modified SAPO-34 Zeolite Membranes

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Abstract

The global concern to reduce carbon dioxide (CO_2) gas emission urges the need to explore for the effective membrane separation technology. Gas permeation properties of the membranes are good indicator in reflecting the gas mixture's separation performance of the membranes. Nowadays, silicoaluminophosphate-34 (SAPO-34) zeolite membrane is gaining increasing popularity among researchers in gas permeations studies due to their small pore structure. In current study, the synthesized SAPO-34 zeolite membrane was modified with Ba^{2+} cation to form Ba-SAPO-34 membrane. CO_2 and CH_4 gas permeation studies for the Ba-SAPO-34 zeolite membrane were carried out at temperature of 30 – 180 ^oC and pressure difference of 100 – 500 kPa. The effect of temperature and pressure difference on the gas permeation properties of the Ba-SAPO-34 zeolite membranes was investigated. When the pressure difference was increased from 100 to 500 kPa at 30 ^oC, the CO_2 flux and CH_4 flux increased from 19.5 to 78.7×10^{-3} mol/m^2·s and from 0.35 to 1.75×10^{-3} mol/m^2·s respectively. When the temperature was increased from 30 to 180 ^oC at pressure difference of 100 kPa, the CO_2 flux decreased from 19.5 to 9.8×10^{-3} mol/m^2·s but the CH_4 flux remained nearly constant at 0.35×10^{-3} mol/m^2·s. CO_2/CH_4 ideal selectivity as high as ~56 was obtained for Ba-SAPO-34 membrane's gas permeation at 30 ^oC and 100 kPa pressure difference.

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Keywords: Ba-SAPO-34; zeolite membrane; gas permeation; CO_2; CH_4

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1. Introduction

The emission of carbon dioxide (CO_2), as greenhouse gas, to atmosphere is one of the major environmental issues nowadays. The drawbacks of increasing concentration of greenhouse gas in the atmosphere include rise in global temperature and increase in sea levels which might disturb the ecosystem. Therefore, the global concern to reduce carbon dioxide (CO_2) gas emission urges the efforts among researchers to seek for different technologies which can efficiently achieve the goal. Among the worldwide concerns to restrict CO_2 emission from large emission sources, CO_2 removal from methane gas (CH_4) is gaining popularity nowadays. Numbers of articles were published by different researchers aimed at reporting various technologies for recovery and separation of CO_2 [1–5]. Conventionally, technologies include absorption and adsorption are used for CO_2 separation and recovery [6, 7]. Nevertheless, problems brought by these conventional technologies includes high energy consumption, unit operation complexity and equipment corrosion problem [8, 9].

Owing to the limitations brought by conventional technologies, membrane technologies become a potential alternative for gas permeation and separation. The type of common organic membranes widely studied for gas permeation and separation is polymer membranes due to its low cost and relatively easier preparation. However, the application of polymer membranes is limited by its low chemical, thermal and mechanical strength [10–12].

Apart from organic membrane, inorganic membranes such as zeolite membranes are promising candidate for gas permeation and separation. Zeolite membranes possess advantages include well-defined pore size, high thermal and chemical stability [13, 14]. Extensive studies have been performed aimed at investigating potential of zeolite membranes for gas permeation and separation [12, 15–20]. In recent years, small pore zeolite membrane such as silicoaluminophosphte-34 (SAPO-34) has drawn increasing attention among researchers in their research works focusing in gas permeation and separation [6, 17, 21–22]. In addition, ion exchange is one of the methods to improve the gas permeation and separation of zeolite membrane. In our previous work [23], H-SAPO-34 membranes were synthesized and ion-exchanged with Ba^{2+} cation. The Ba-SAPO-34 displayed improved CO_2/CH_4 selectivity compared to H-SAPO-34 zeolite membrane [23].

In current study, Ba-SAPO-34 zeolite membrane was prepared. CO_2 and CH_4 gas permeation studies for the Ba-SAPO-34 zeolite membrane were carried out at temperature of 30 – 180 ^oC and pressure difference of 100 – 500 kPa. The effect of temperature and pressure difference on the gas permeation properties of the Ba-SAPO-34 zeolite membranes was investigated.

2. Materials and Methods

2.1. Preparation of Membrane

The SAPO-34 membrane was deposited on α -alumina disc with diameter of 25 mm. The SAPO-34 membrane was then modified to Ba-SAPO-34 membrane by using Ba^{2+} cation according to the procedures described in our previous work [23]. The characterization results of the Ba-SAPO-34 membrane were described in our previous work [23].

2.2. Gas Permeation Studies

The Ba-SAPO-34 membrane, placed in a stainless steel module, was subjected to single gas permeation studies. The stainless steel module, with Ba-SAPO-34 membrane inside, was placed in a fabricated oven during the single gas permeation studies. Mass flow controller was used to feed pure CO_2 or CH_4 gas to the membrane. The retentate stream of the membrane was closed and the permeate stream flow was measured using bubble flow meter. During the permeation study, the pressure difference across the membrane was varied from 100 to 500 kPa by keeping the permeate pressure at atmospheric pressure. By using the oven where the stainless steel module was placed, the gas permeation temperature was varied from 30 to 180 ^oC.

Flux, J_i (mol/m^2.s) of component gas *i* (CO_2 or CH_4 in current study) was calculated as shown in Equation (1).

$$J_i = \frac{n_i}{A \cdot t} \tag{1}$$

where $\frac{n_i}{t}$ is the molar flow rate of component *i* (mol/s), A is the effective permeation area of the membrane (m^2).

Permeance, P_i (mol/m^2.s.Pa) of component gas *i* (CO_2 or CH_4 in current study) was calculated as shown in Equation (2).

$$P_i = \frac{J_i}{\Delta p_i} \tag{2}$$

where Δp_i is the pressure difference of component *i* across the membrane (Pa).

The CO_2/CH_4 ideal selectivity of the membranes, $\alpha_{CO_2/CH_4}^{ideal}$ was calculated from the ratio of single gas permeances as shown in Equation (3).

$$\alpha_{CO_2/CH_4}^{ideal} = \frac{P_{CO_2}}{P_{CH_4}} \tag{3}$$

3. Results and Discussion

Figure 1 shows the effect of pressure difference on CO_2 and CH_4 gas fluxes through Ba-SAPO-34 membrane for different temperatures. In current study, CO_2 gas fluxes obtained was higher than CH_4 gas fluxes. The higher CO_2 gas fluxes compared to CH_4 in current study can be explained by the combined effect of surface diffusion and micropore diffusion [24]. CO_2 possesses kinetic diameter of ~0.33 nm, which is smaller than the kinetic diameter of CH_4 (~0.38 nm). Hence, the diffusion of CO_2 through the Ba-SAPO-34 micropore framework is easier compared to CH_4. In addition, the surface diffusion of CO_2 through SAPO-34 pore framework is higher than CH_4 due to higher adsorption strength of CO_2 on Ba-SAPO-34 pore framework [25]. It was observed from Figure 1 that both CO_2 and CH_4 gas fluxes increased with increase of pressure difference from 100 to 500 kPa for the temperature range (30 – 180 ^oC) studied. This was due to the increase in the gradient of adsorbed concentration when the pressure difference was increased [26]. Therefore, when the pressure difference was increased from 100 to 500 kPa at 30 ^oC, the CO_2 flux and CH_4 flux increased from 19.5 to 78.7×10^{-3} mol/m^2·s and from 0.35 to 1.75×10^{-3} mol/m^2·s respectively.

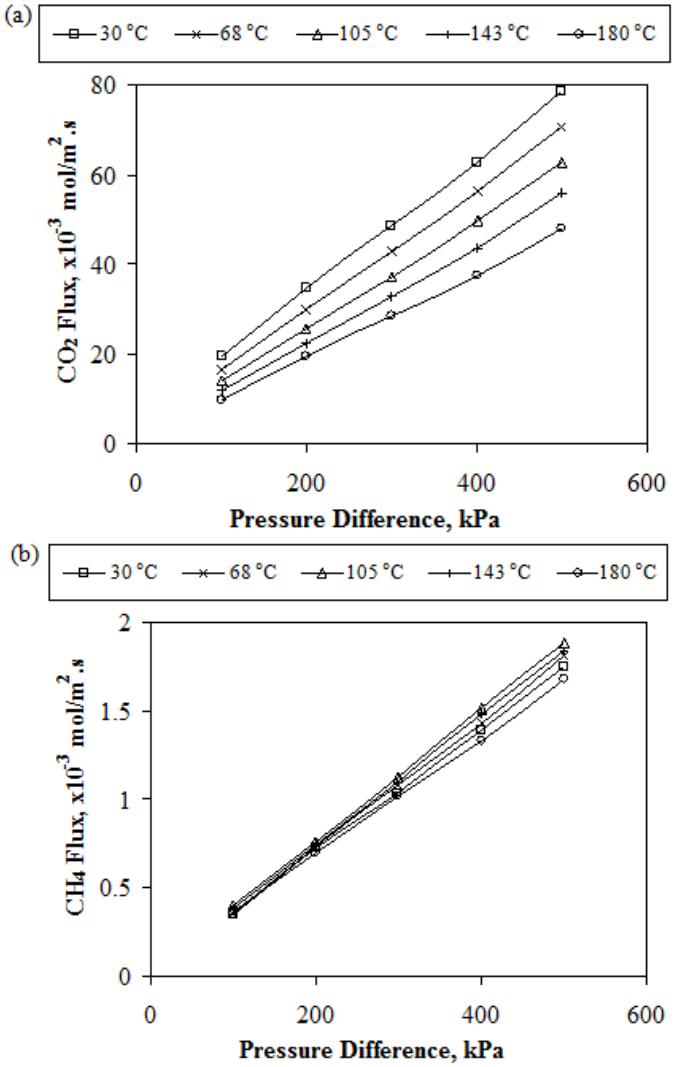

Fig. 1. Gas fluxes of (a) CO_2 and (b) CH_4 through Ba-SAPO-34 membrane as a function of pressure difference for different temperatures

Besides, the CO_2 gas flux decreased with increase in temperature as observed in Figure 1(a). This was due to reduction in CO_2 surface coverage on Ba-SAPO-34 pore framework when the temperature was increased from 30 to 180 ^{o}C [6]. When the temperature was increased from 30 to 180 ^{o}C at pressure difference of 100 kPa, the CO_2 flux decreased from 19.5 to 9.8×10^{-3} mol/m^2·s. It was interesting to observe that for all the pressure differences (100, 200, 300, 400 and 500 kPa) studied, increase in temperature from 30 to 105 ^{o}C led to rise in CH_4 gas fluxes, but further increase in temperature from 105 to 180 ^{o}C resulted in drop in CH_4 gas fluxes. Generally, increase in temperature causes decrease in surface diffusion but increase in micropore diffusion. The increase in temperature from 30 to 105 ^{o}C enhanced the CH_4 micropore diffusion through the pore but decreased the CH_4 surface coverage. The combination of these two effects resulted in increase in CH_4 gas fluxes when temperature was increased from 30 to 105 ^{o}C. Anyway, increasing the temperature beyond 105 ^{o}C caused decrease in CH_4 gas fluxes. This was because the decline in surface coverage prevailed over the increase in micropore diffusion of CH_4 when the temperature was increased from 105 to 180 ^{o}C [27]. Consequently, increase in temperature from 30 to 180 ^{o}C at

pressure difference of 100 kPa produced overally a nearly constant CH_4 flux of 0.35×10^{-3} mol/m^2·s.

Figure 2 shows the effect of temperature on the CO_2/CH_4 ideal selectivities of Ba-SAPO-34 membrane. Ideal selectivities were calculated from the ratio of the single gas permeances in current study. Gas permeances were calculated as the gas fluxes per unit pressure difference. Similar to changes of gas fluxes as shown in Figure 1, CO_2 single gas permeance decreased but CH_4 single gas permeance remained nearly constant when the temperature was increased from 30 to 180 ^oC. Consequently, the CO_2/CH_4 ideal selectivities decreased when the temperature was increased from 30 to 180 ^oC as shown in Figure 2. CO_2/CH_4 ideal selectivity as high as ~56 was obtained for Ba-SAPO-34 membrane's gas permeation at 30 ^oC and 100 kPa pressure difference, which was comparable with the CO_2/CH_4 ideal selectivity of 32-95 reported by Li et al. [25] for SAPO-34 membranes at 22 ^oC and pressure difference of 138 kPa.

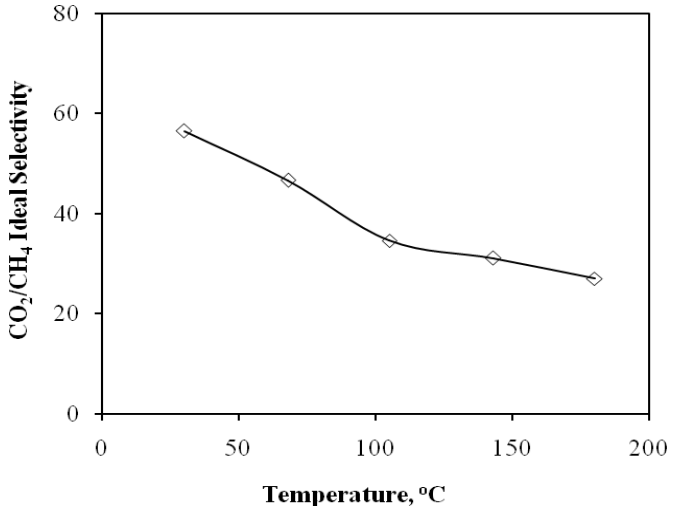

Fig. 2. CO_2/CH_4 ideal selectivities of Ba-SAPO-34 membrane as a function of temperatures at pressure difference of 100 kPa

Figure 3 shows the effect of temperature on the percentage drop in CO_2/CH_4 ideal selectivities of Ba-SAPO-34 membrane. As shown in Figure 3, the percentage drop in CO_2/CH_4 ideal selectivities was ~52 % when the temperature was increased from 30 to 180 ^oC at pressure difference of 100 kPa. When the pressure difference was increased in current study, the CO_2 gas permeances decreased because the increase in gradient of adsorbed concentration was lower than the increase in CO_2 pressure difference. However, CH_4 single gas permeance remained nearly constant with increase in pressure difference. Therefore, the CO_2/CH_4 ideal selectivity (which is ratio of CO_2 single permeance to CH_4 single gas permeance) decreased when pressure difference was increased in current study. In addition, the percentage drop in CO_2/CH_4 ideal selectivities with increase in temperature was lower when the pressure difference was higher as shown in Figure 3.

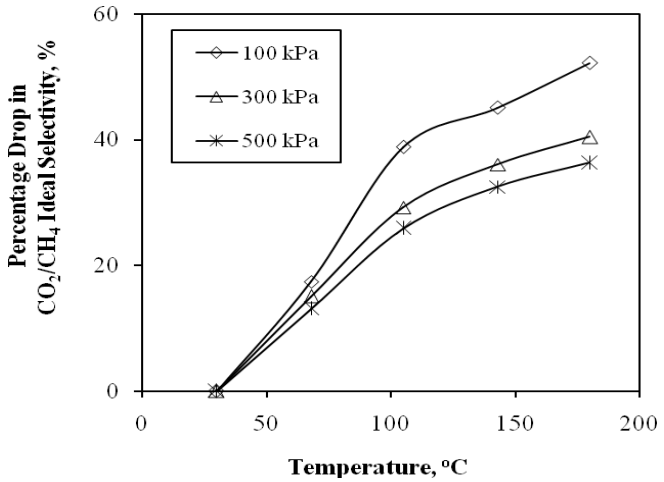

Fig. 3. Percentage drop CO_2/CH_4 ideal selectivities of Ba-SAPO-34 membrane as a function of temperatures

4. Conclusions

In current study, the synthesized SAPO-34 zeolite membrane was modified with Ba^{2+} cation to form Ba-SAPO-34 membrane. CO_2 and CH_4 gas permeation studies for the Ba-SAPO-34 zeolite membrane were carried out at temperature of 30 – 180 °C and pressure difference of 100 – 500 kPa. The effect of temperature and pressure difference on the gas permeation properties of the Ba-SAPO-34 zeolite membranes was investigated. In current study, CO_2 gas fluxes obtained was higher than CH_4 gas fluxes for all the range of temperature and pressure difference studied. This was due to the combined effect of surface diffusion and micropore diffusion. When the temperature was increased from 30 to 180 °C at pressure difference of 100 kPa, the CO_2 flux decreased from 19.5 to 9.8×10^{-3} mol/m^2·s due to reduction in CO_2 surface coverage on Ba-SAPO-34 pore framework. The CO_2 flux and CH_4 flux increased from 19.5 to 78.7×10^{-3} mol/m^2·s and from 0.35 to 1.75×10^{-3} mol/m^2·s respectively when the pressure difference was increased from 100 to 500 kPa at 30 °C. CO_2/CH_4 ideal selectivity as high as ~56 was obtained for Ba-SAPO-34 membrane's gas permeation at 30 °C and 100 kPa pressure difference.

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